COFFEE AND ESTIMATION OF ITS VALUE.

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IN volume II, page 50 (1887–'88), of the Proceedings of the Kansas Academy of Science, there is published an article by the author on the alkaloidal strength of teas. In answer to the question, Is the alkaloidal strength of tea an index of its commercial value? it was shown that a negative answer to this question must be given; that the alkaloidal strength has no relation to the commercial price. For example, it was shown that a tea rated at 25 cents per pound contained 2.49 per cent. of theine, while a tea at 90 cents per pound contained 3.73 per cent. of theine, and that a tea at 60 cents per pound contained 3.67 per cent. of theine, showing that commercial price was no index to alkaloidal strength. Applying the same question to coffee, we have found the same to be true. A fine Mocha will contain about 0.64 per cent., while another of a different variety, and about the same price, will contain 1.53 per cent of caffeine.

In determinations of caffeine from coffee recently made in our laboratory, it has been found that the percentage of caffeine in coffee varies considerably according to the locality where it has been cultivated. Some coffees have ranked as high as 1.97 per cent. of alkaloid, while it is very commonly the case that an excellent coffee, commanding a good price, will yield as low as 0.8 per cent. of the alkaloid. The importance of this fact has never been applied as it might be, as there are some to whom the stimulating effect of caffeine is undesirable, while there is at the same time a demand for a beverage that shall have an agreeable taste. On the other hand, there are others to whom the stimulating effect of caffeine may be an advantage. The quality of roasted coffee is dependent mainly upon the substances which occasion the peculiar aroma. These substances have thus far been practically unknown. Erdmann, in *Berichte der Deutschen Chemischen Gesellschaft*, 1903, refers to the oil of coffee which has been obtained by treating roasted coffee with steam. The yield from 150 kilograms of roasted and ground Santos coffee was 83.5 gm., or 0.055 per cent., of an oil of a brown color, of a specific gravity of 1.0844, and a strong odor of coffee. On distillation of the oil, the greater portion passed over between 150 and 190° C. in the form of a light-colored oil. This contained furfur

alcohol, and much valerianic acid. The constituent having the characteristic aroma of coffee is said to be nitrogenous and not a phenol, as has been assumed heretofore. The exact isolation has not been possible so far. It is well known that the roasting of coffee carries with it antiseptic and deodorant properties. This is evidently inherent in the volatile products of roasted coffee, and possibly due to phenols present in these volatile products.

Our own experiments in the investigation of the volatile aromatic constituents of roasted coffee have led us to the conclusion that these when isolated are extremely volatile. For example, when chloroformic and petroleum ether solutions of the coffee are evaporated at extremely low temperatures it is found that the aroma evaporates and diffuses through the air at a lower temperature than that at which the ethereal liquids evaporate. We have endeavored, therefore, to resort to another method of recovering the volatile aromatic oil, which consisted in placing in a retort 500 gm. of finely powdered coffee and connecting the retort with a condenser and two receivers in tandem, the first receiver being refrigerated with ice and salt and the second refrigerated with liquid air. Only a few drops of a colorless liquid was recovered from the dry distillation in the second receiver. It is nearly colorless and has an odor suggesting that of capronic acid. It is very powerful and penetrating, diffuses very rapidly in the air, and when highly diluted with atmospheric air suggests the odor of coffee. The distillate obtained in the first receiver, of a yellowish-brown color, has an ammoniacal odor. But it is evident that the characteristic aroma of roasted coffee is due to a mixture of different compounds not obtained by any such process. We have not been able to pursue further this investigation, but hope at some future time to recover a sufficient amount of the distillate mentioned to purify the same and to make an analysis of it. The claim that oil of coffee may be obtained by distilling coffee with steam under pressure and collecting the distillate by means of ether and then evaporating the ethereal solution does not seem to us to be well founded, as we have not been able to obtain a volatile oil by this process which has the suggestion of the aroma of coffee. As we have said, ethereal and chloroformic solutions of the volatile products usually leave behind on evaporation little or no residue that are characteristic of the aromatics in coffee, these aromatics becoming evaporated on evaporation of the solvent, even though the solvent is evaporated at a very low temperature.

ANALYSIS.

In the analysis of coffee we have as yet no standard that would estimate the value of coffee from the commercial standpoint. The bureau of chemistry of the United States Department of Agriculture, in its standard for this beverage, makes the following statements:

1. Coffee is the seed of *Coffea arabica* L. or *Coffea liberica* Bull., freed from all but a small portion of its spermoderm, and conforms in variety and place of production to the name it bears.

2. Roasted coffee is coffee which by the action of heat has become brown and developed its characteristic aroma; it contains not less than ten per cent. of fat and not less than three per cent. of ash.

In Bulletin No. 90 of the bureau of chemistry of the Department of Agriculture, page 43, there are two processes mentioned for the determination of caffeine and caffeotannic acid, which I hereby transcribe:

Caffeine.

Method of Hilger and Fricke (*a*).—Take 5 to 10 grams of coffee, add 100 cc. of water, and boil, filter, and treat the residue twice more with boiling water. Add to the united filtrates an excess of lead acetate, filter, and wash. Treat the filtrate with hydrogen sulfid to remove the excess of lead, filter, wash, and evaporate the filtrate to dryness in a Hoffmeister schälschen with some sand and a little magnesia. Crush the schälschen between filter-paper, place in a continuous-extraction apparatus, and extract with chloroform until exhausted. Dry the chloroform extract at 100 degrees and weigh as caffeine. If the caffeine does not appear to be pure, determine the nitrogen in the residue by the Gunning method. $N \times 3.464 =$ caffeine.

Caffeotanic Acid.

Krug's method (*b*).—Treat two grams of the coffee with 10 cc. of water and digest for thirty-six hours, add 25 cc. of 90 per cent. alcohol and digest twenty-four hours more, filter, and wash with 90 per cent. alcohol. The filtrate contains tannin, caffeine, color, and fat. Heat the filtrate to the boiling-point and add a saturated solution of lead acetate. If this is carefully done a caffetannate of lead will be precipitated, containing 49 per cent. of lead. As soon as the precipitate has become flocculent, collect on a tared filter, wash with 90 per cent. alcohol until free from lead, wash with ether, dry, and weigh. The precipitate has the following composition: $Pb_3C_{15}H_{18}O_{82}$. The weight of the precipitate multiplied by 0.51597 gives the weight of the caffeotannic acid.

Dr. Wilhelm Autenrieth, in his work on the detection and estimation of alkaloidal substances, page 185, gives a résumé of the literature on the estimation of caffeine of caffeine-bearing plants, and gives six different methods. We have tried these various methods, and have found the Katz method to be the most satisfactory. This method is as follows:

Shake 10 grams of powdered coffee or tea for thirty minutes with 200 grams of chloroform and 5 grams of ammonium hydroxid solution. When the liquid has settled filter 150 grams of the chloroform solution, which should be perfectly clear and free from water. Distil the chloroform and dissolve the residue with gentle heat in about 6 cc. of ether. Add 20 cc. of 0.5 per cent. of hydrochloric acid and, in an assay of coffee, also 0.2 to 0.5 grams of solid paraffin. Evaporate the ether and filter the cold, aqueous solution. Wash the flask and filter-paper a few times with small portions of 0.5 per cent. hydrochloric acid. Finally extract the total aqueous hydrochloric acid solution four times with 20 cc. portions of chloroform. Distil the filtered chloroform extracts, dry the residue, and weigh. This residue will consist of nearly pure caffeine.

The one difficulty in all of these processes is that the caffeine recovered in the process contains some coloring matter or some empyreumatic matter imparting color to the product. It has been suggested that when the yield is thus contaminated the crystals be subjected to the Kjeldahl's nitrogen determination. The quantity of anhydrous caffeine is calculated on the basis of this analysis. One cc. of $\frac{N}{10}$ oxalic acid represents 0.00485 grams of anhydrous caffeine. Tetrachlormethane has been suggested by some analysts as a proper substitute for chloroform in the extraction of the alkaloid. We have found that an almost colorless caffeine can be obtained by properly using this solvent. It has been our endeavor to obtain a simple process by which we could estimate the caffeotannic acid and the caffeine at the same time. We have thus far had quite accceptable results by using a modification of the Krug method. Instead of using 2 gm. of the coffee, 7 gm. of the finely powdered coffee are taken. After digestion with the water and alcohol (as required by the formula) for twenty-four hours, 100 cc. of the filtrate, which is made to represent 5 gm. of the coffee, are taken. This is precipitated by the solution of lead acetate, and 60 cc. of the filtrate, representing 3 gm. of the coffee, are taken and treated with an excess of diluted sulfuric acid. The filtrate from the lead sulfate, which has been thoroughly washed, is carefully evaporated to remove traces of alcohol, and the residue is filtered into a separatory funnel and thoroughly washed with 15,

10, 10 and 5 cc. of chloroform, added in succession to the aqueous solution. The mixed chloroformic solutions are then evaporated to dryness and the resulting crystals of caffeine, if they contain an appreciable amount of coloring matter, are redissolved in a mixture of petroleum, ether, and chloroform, which gets rid of small quantities of color. This latter solution when filtered is evaporated and the crystals are weighed, and from the weight the percentage of alkaloid computed. The results that we have thus far obtained show concordant results. Samples of roasted coffee as obtained upon the market have given from 0.825 to 1.66 per cent. of caffeine, and of caffeotannic acid (or plant acids estimated as caffeotannic acid) from 10 to 12.8 per cent.

We desire to append to the present article the analysis of samples of coffee of different varieties which we have collated from the Proceedings of the American Pharmaceutical Association, volume 24, page 144, and, for the benefit of those who are interested in assay, we would call attention to the tables which accompany the most excellent article on the chemical constituents of coffee presented in Bulletin No. 90 of the Department of Agriculture, pages 43 to 45, inclusive.

ANALYSES OF SAMPLES OF COFFEE.

VARIETIES.	Caffeia.....	Fat.....	Mucilage...	Caffeotannic acid...	Cellulose....	Ash.....	Potassa.....	Phosphorus.
Finest plantation Jamaica.....	1.43	14.76	25.3	22.7	33.8	3.8	1.87	0.31
Finest green Mocha.....	0.64	21.79	22.6	23.1	29.9	4.1	2.13	0.42
Pearl plantation Ceylon.....	1.53	14.87	23.8	20.9	36.0	4.0	....	0.27
Washed Rio.....	1.14	15.95	27.4	20.9	32.5	3.5	....	0.51
Costa Rica.....	1.18	21.12	20.6	21.1	33.0	4.9	....	0.46
Malabar.....	0.88	18 80	25.8	20.7	31.9	4.3	....	0.60
East India.....	1.01	17.00	24.4	19.5	36.4	....	....	....

Proc. Am. Pharm. Ass'n, vol. 24, p. 144.

Paul and Cownley proved that a small amount of caffeine is lost in the roasting of coffee. To illustrate this, three samples are given: First, one roasted to extreme degree; second, one just far enough to give berries a fine chestnut-brown color; third, coffee roasted to pale brown color, when aroma was not fully developed.

COFFEE.	Loss of weight in roasting.	In raw coffee.	In roasted coffee.	
			Found.	E timated.
Low roasted.....	13.7%	1.10%	1.30%	1.28%
Medium roasted.....	16.0	1.10	1.36	1.31
High roasted.....	31.7	1.10	1.25	1.61

Proc. Am. Pharm. Ass'n, vol. 35, p. 142.

Julian E. Walker gives his results of the analysis of several kinds of roasted coffee for percentage of caffeine in different sorts:

Java	0.89%
Siberian Java	1.08
Salvador	1.01
Costa Rica	1.24
Mocha	0.54
Peaberry or Fenroll	0.77
Rio	1.12

Proc. Am. Pharm. Ass'n, vol. 38, p. 446.

ANALYTICAL RESULTS EMPLOYING VARIOUS SORTS.

W. T. A. Warner examined a large number of coffees in the laboratory of the colonial museum at Haarlem, conducting his researches with particular reference to the Siberian coffee cultivated in Java as a substitute for Arabian coffee:

Samples of Siberian Coffee.	H_2O Ext.	C_2H_5OH ext., per cent.	Fat, per cent.	Caffeine, per cent.	Ash, per cent.	Phosphoric acid in ash, per cent.	Potash in ash, per cent.
Sindjas	32.92	17.43	12.26	1.29	3.87	8.95	72.05
Timor	32.05	16.60	13.23	1.11	3.96	7.87	78.78
Banthain	30.38	18.89	14.78	1.11	4.29	10.26	77.83
Boengi	31.09	18.41	16.10	1.03	3.88	12.37	71.47
Loewae	30.13	17.82	16.06	1.48	4.30	11.25	79.90
Waloe Pengenten	26.98	17 85	13.57	1 25	3.97	9.47	76.91
Kaui Redjo	29.59	18.89	15 43	1.00	3.74	10.67	? rep.
Taman, Tjiasem	30.47	19.91	16.48	1.39	4.09	10.27	67.57
Malang	30.21	19.81	16.36	1.07	4.11	11.08	63.82
Averages	30.00	.....	15.00	1.00	4.00	.....	.....

The water extract was obtained by boiling five minutes with distilled water; the alcohol extract, by boiling during half an hour with ninety-five per cent. alcohol; the fat, by extraction with ether; the alkaloid, by one of three methods, viz., van Romburgh's, van Ledden-Hulseboch's, and George's, preference being given to van Romburgh's method, which consists in shaking out the aqueous extraction, after addition of lead acetate with chloroform.

The following table gives a comparison of raw and roasted Java-Arabia and Java-Siberia coffees. The extracts, unless otherwise indicted, are obtained by the action of each solvent on fresh portions of the same coffee. The coffees represent good qualities of the market during 1898.

	Raw Malang, per cent.	Roasted Malang, per cent.	Raw Liberia, per cent.	Roasted Liberia, per cent.
Aqueous extract	33.52	27.40	35.16	34.17
Alcoholic extract	19.38	16.12	18.62	17.27
Ether-alcoholic extract	17.70	16.53	15.80	15.92
Chloroform extract	15.65	17.91	13.88	15.10
Ether extract	13.63	14.20	12.19	13.13
Petroleum ether extract	12.51	14.31	10.84	11.68
Ether extract after petroleum ether	1.08	4.74	0.75	3.14
Chloroform extract after petroleum ether	1.08	1.41	1.18	2.60
Alcohol extract after petroleum ether	3.14	5.37	8.68	2.79
Nitrogen	2.83	2.77	2.73	2.89
Caffeine	1.16	1.57	1.59	2.19
Albuminoids	15.74	14.71	14.43	14.42
Cellulose	28.75	20.47	26.68	15.32
Pentoses	5.14	3.15	5.01	2.44
Ash	4.46	4.83	4.02	4.37
Water	11.24	5.64	11.40	3.98

Proc. Am. Pharm. Ass'n, vol. 48, p. 608.

CHASE & SANBORN COFFEE.

Ash, sample No. 1.. 3.98 per cent.
" " No. 2.. 3.92 "
" " No. 3.. 3.96 "

Total..... 11.86 per cent.

Average..... 3.95 per cent.

Samples:

A..... 0.196 per cent.
B..... 0.194 "
C..... 0.192 "

Av. moisture, 0.194 in 10 grams.
Present moisture, 1.94 per cent.

Ash:

3.89 per cent.
4.096 "
4.046 "
3.142 "

Av., 3.996 per cent.

Fat (Chase & Sanborn):

	Fat.	
50 gr.	8.0505 = 16.101	per cent.
50 gr.	8.0980 = 16.196	"
50 gr.	8.0275 = 16.055	"
50 gr.	7.8708 = 15.7416	"
50 gr.	7.9270 = 15.8540	"